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High-Performance Fibers to Imidazole and Derivatives

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Cross References

High-Pressure Technology, treated in B4 High-Tech Ceramics → Ceramics, Advanced Structural Products High-Temperature Composites → Composite Materials; → Metallic-Matrix Composites High-Temperature Fibers \rightarrow High-Performance **Fibers** High Temperature Plastics → Specialty Plastics High-Tenacity Fibers → High-Performance **Fibers** Histamine Antagonists →Antiallergic Agents; Antacids and Peptic Ulcer Treatment Histidine → Amino Acids Hollow-Fiber Membranes → Membranes and Membrane Separation Holmium → Rare Earth Elements Hydroboranation → Boron Compounds Hydrobromic Acid → Bromine Compounds Hydrocarbon Oxidation → Oxidation Hydrocarbon Resins → Resins, Synthetic

Hydroformylation → Oxo Synthesis

Hydrogen Bromide → Bromine Compounds Hydrogen Chloride → Hydrochloric Acid Hydrogen Cyanide → Cyano Compounds Hydrogen Economy → Hydrogen Hydrogen Fluoride → Fluorine Compounds, Inorganic Hydrogen Iodide → Iodine Hydrogen Selenide → Selenium and Selenium Compounds Hydrogen Storage Alloys → Hydrides Hydrometallurgy → Metallurgy Hydroxyanthraquinones →Anthraquinone Dyes Hydroxybenzaldehyes → Benzaldehyde Hydroxyhydroquinone → Phenol Derivatives Hypochlorous Acid → Chlorine Oxides and Chlorine Oxygen Acids Hypoglycemic Drugs →Antidiabetic Drugs Hydrophosphorus Acid → Phosphorus Compounds, Inorganic Illites → Clays

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cobalt- or rhodium-phosphin complexes are used.

Propen is the olefin mostly used. The oxoproducts are converted to alcohols, carboxylic acids, aldol-condensation products, and primary amines. About 20 commercial processes are state of the art. An excellent review is given in [8.41] (see → Oxo Synthesis).

Homologation. Under the reaction conditions of the hydroformylation alcohols and aldehydes react with carbon monoxide – hydrogen under elongation of the chain by one CH₂- unit

$$R-CH_2-OH+CO/H_2--$$

 $R-CH_2-CH_2-OH+H_2O$

Homologation has been performed with a number of alcohols, the production of ethanol from methanol has been most intensively investigated. The homologation is not used industrially because of the many side reactions which take place [8.42].

Synthesis Gas as Chemical Feedstock. Hydrogen—carbon monoxide mixtures, hydrogen alone, and their primary product methanol are important feedstocks for the chemical industry. Nowadays, ethylene which is produced from propane, ethane, naphtha, or gas oil is the most important feedstock for the production of industrial organic chemicals in the chemical industry. Bascially, it is, however, possible to obtain these compounds from synthesis gas thus changing the feedstock basis to coal (see Fig. 100).

8.1.5. Hydrogen in Organic Synthesis

Hydrogen is required for the production of chemicals and intermediates in organic chemistry. A large number of hydrogenations or reductions are carried out on a technical scale (

Hydrogenation and Dehydrogenation).

Activated and nonactivated double and triple bonds in olefins and acetylenes can be easily partially or totally hydrogenated, whereas the hydrogenation of aromatic and heterocyclic bonds requires more energetic conditions. Functional groups, such as carbonyl, nitro, nitroso, and nitrile groups, can also be hydrogenated.

The reaction conditions are dictated by equilibrium (65). The reactions are exothermal and run in the presence of a catalyst.

$$A + nH_2 \longrightarrow BH_{2n} \tag{65}$$

Directions for carrying out catalytic hydrogenations on a laboratory or industrial scale are given in [8.43]. Summaries of hydrogenation reactions are given in [8.44] and [8.45]. Hydrogenation catalysts are metals of groups 8-10 of the periodic system (see front matter of this volume), e.g., Raney nickel, as well as copper and molybdenum. In particular the noble metals (Pt, Pd), are highly-active catalysts [8.46]. Homogeneous systems with molecularly dispersed catalysts in the solution, can be used for special synthesis problems (selective hydrogenation, asymmetric synthesis) but are at present of no great importance in commercial areas because of the frequently encountered difficulty to remove the catalyst from the reaction mixture. Table 40 gives an

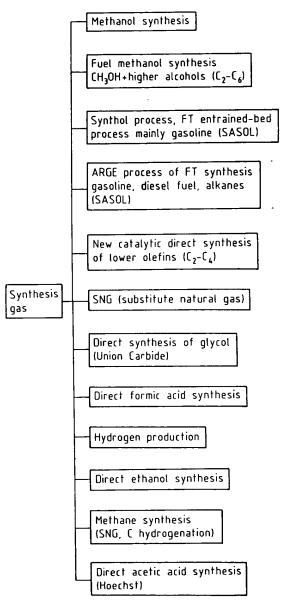


Figure 100. Synthesis gas as feedstock in the chemical industry

Table 40. Selection of important industrial hydrogenation reactions

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middle pressure hydrogenation over Ni-Pt-Li-Al-5, catalyst in liquid phase (UOP, DSM, Thoray, Houdry) Thoray, Houdry Thoray, Thoray Thoray, Thoray Thoray, Thoray, Thoray Thoray, Houdry Thoray, Thoray, Thoray Thoray, Thoray Thoray, Thoray, Thoray Thoray, Thoray Thoray, Thoray Thoray, Thoray Thoray, Thoray Thoray, Thoray	Reaction	Product	Drogen Contract		1
cyclobexane middle pressure hydrogenation over starting material for nylon production Ni-Pt-Li-Al-JO, cutalyst in liquid phase (UOP, DSM, 1Ph. Li-Al-JO, cutalyst in liquid phase hydrogenation (cyclobexanone/ol. adipic acid, caprolaction 25-30 MPa/T0-100°C over Raney inckel incheb bed. 20 MPa, 180–200 °C Ni catalyst printed butanediol rickel butanediol rickel butanediol rickel butanediol sas phase hydrogenation at 2-0.3 MPa/ aromatics extraction solvents, sour gas, sulfolane Shell process, 11000 (µ aromatics extraction solvents, plasticizers, sumply base hydrogenation at 2-0.3 MPa/ components for solvents, plasticizers, catalyst catalyst suppression over Raney nickel catalyst suppression which butanediol Mitsubishi, Kato Ind. (Japan) process methyl-cyclo-hexane	Hydrogenation of unsaturated hydrocarbons and accounting	1000	riocess icatures	Uses	1
Harry Hourty Branch (UOP, DSM, Iam), solvent Thoray Houdry) Du Pont (300°C), liquid phase hydrogena- tion 25-30 MPa/70-100 °C over Rancy a-OH butanediol trickhe bed, 20 MPa, 180–200 °C Ni catalyst sulfolane Shell process, 11 000 t/a	$\bigcirc + 3 H_2 \longrightarrow \bigcirc$	cyclohexane	middle pressure hydrogenation over Ni-/Pt-Li-Al ₂ O ₃ catalyst in liquid phase	starting material for nylon production (cyclohexanone/ol, adipic acid, caprolac-	ı
H ₂) ₄ – CN adiponitrile de d. 20 MPa, (700°C), liquid phase hydrogenary linekel bed. 20 MPa, (180–200°C Ni catalyst nent, solvent aromatics extraction solvents, sour gas, sulfolanc Shell process, 11 000 t/a aromatics extraction solvents, sour gas, sulfolanc Shell process, 11 000 t/a aromatics extraction solvents, sour gas, sump phase hydrogenation at 2–0.3 MPa/ 115°C, Ni catalyst sump phase hydrogenation, 8 MPa/115°C Ni catalyst catalyst sump phase hydrogenation (up to 30 MPa, 25–130°C), Raney nickel catalyst buttanediol Mitsubishi, Kao Ind. (Japan) process his-(hydroxy-methyl)-cyclo-methyl)-cyclo-methyl)-cyclo-hexane	(analogous: cyclohexanol from phenol, cyclohexane carboxylic acid from benzoic acid)		(11.1.) Milsubishi) gas phase (UOP, DSM, Thoray, Houdry)	tam), solvent	droge
nickel butanediol trickle bed, 20 MPa, 180–200 °C Ni catalyst sulfolanc Shell process, 11 000 t/a scrubbing agent aromatics extraction solvents, sour gas, aromatics ex	$CN - CH_2 - CH = CH - CH_2 - CN + H_3 - CN - (CH_2)_4 - CN$	adiponitrile	Du Pont (300 °C), liquid phase hydrogenation 25 · 30 MPa/70 · 100 °C over Raney	hexanediamine	
sulfolanc Shell process, 11 000 t/a aromatics extraction solvents, sour gas, scrubbing agent oxo-alcohols gas phase hydrogenation at 2–0.3 MPa/ 115°C, Ni catalyst sump phase hydrogenation, 8 MPa/115°C Ni catalyst catalyst Primary amines hydrogenation (up to 30 MPa, 25–130°C), Raney nickel catalyst buttancdiol Mitsubishi, Kato Ind. (Japan) process bis-(hydroxy-methyl)-cyclo-methyl)-cyclo-methyl-cyclo-methyl)-cyclo-hexane	$OH - CH_2 - C \equiv C - CH_2OH + 2H_2 \longrightarrow OH - (CH_2)_4 - OH$	butanediol	nickel trickle bed, 20 MPa, 180–200 °C Ni catalyst	Dolvesters polyurethane placticing	
oxo-alcohols gas phase hydrogenation at 2–0.3 MPa/ components for solvents, plasticizers, 115°C, Ni catalyst sump phase hydrogenation, 8 MPa/115°C Ni catalyst catalyst primary amines hydrogenation (up to 30 MPa, 25–130°C), Raney nickel catalyst butanediol Mitsubishi, Kato Ind. (Japan) process bis-(hydroxy-two step Eastman-Kodak process methyl)-cyclo-hexane	$\left\langle \bigcap_{SO_2} + H_1 \longrightarrow \left\langle \bigcap_{SO_2} \right\rangle$	sulfolanc	with Cu-, Cr-promotors Shell process, 11 000 t/a	aromatics extraction solvents, sour gas, scrubbing agent	
oxo-alcohols gas phase hydrogenation at 2–0.3 MPa/ 115 °C, Ni catalyst sump phase hydrogenation, 8 MPa/115 °C, Ni catalyst catalyst primary amines hydrogenation (up to 30 MPa, 25–130 °C), Raney nickel catalyst butancdiol Mitsubishi, Kato Ind. (Japan) process bis-(hydroxy- methyl)-cyclo- hexane	Secure hydrogenation as purification step during production of ethylene, propene, and butadiene Further processing of oxo-products				
primary amines hydrogenation (up to 30 MPa, 25–130°C), Putanediol Mitsubishi, Kato Ind. (Japan) process methyl)-cyclo- hexane	$R - C_{H}^{O} + H_{1} \longrightarrow R - CH_{2}OH$	oxo-alcohols	gas phase hydrogenation at $2-0.3~\mathrm{MPa}/$	COMPONENTS for columns	
primary amines hydrogenation (up to 30 MPa, 25–130 °C), Raney nickel catalyst Raney nickel catalyst butancdiol Mitsubishi, Kao Ind. (Japan) process bis-(hydroxy- two step Eastman-Kodak process methyl)-cyclo- hexane	analogous: ethylhexanol from ethylhexanal)		115°C, Ni catalyst sump phase hydrogenation, 8 MPa/115°C Ni catalyst	detergents	
butancdiol Mitsubishi, Kao Ind. (Japan) process bis-(hydroxy- two step Eastman-Kodak process methyl)-cyclo-	$R - C' + NH_3 + H_2 \longrightarrow R - CH_2 - NH_2$	primary amines	hydrogenation (up to 30 MPa, 25–130°C), Raney nickel catalyst		
bis-(hydroxy- two step Eastman-Kodak process — CH ₂ —OH hexane		butanediol	Mitsubishi, Kao Ind. (Japan) process		
	≻ сн,-он	bis-(hydroxy- nethyl)-cyclo- nexane	two step Eastman-Kodak process		٧

Table 40. (continued)			
Reaction	Product	Process features	Uses
$CH_2 = CH - C + H_2 \longrightarrow CH_2 = CH - CH_2OH$	allylalcohol	Degussa gas phase process (heterogenous catalysis)	starting material for glycerol, glycidol
2 Acetone — mesityl oxide $\xrightarrow{\text{Pd zcolite}} i \cdot \text{Bu} - \overset{Q}{\text{C}} - \text{CH}_3$	MIBK	hydrogenation at Pt-zeolites (modified one step processes)	(extraction) solvent
Fats, oils + $H_2 \longrightarrow R - CH_2 - OH$	fatty alcohols	20-40 MPa/200-400 °C, catalysts of Adkinstype	
$R-O-CH_2CH_2-OH+HCHO+H_2$	polyethylene- glycol ethers	new Hoechst process	sour gas scrubbing agent (Selexol)
Hydrogenation of N-compounds	:	000 0:5/3:10	mutaria mutarial for does nharmaceuticals.
	anilinc	1xed bed hydrogenation over 1xis/Cus, 5co 475°C (Bayer, Allied, Lonza), fluidized bed hydrogenation, 5 MPa/100°C over Cu catalyst (BASF, Cyanamid)	isocyanate polymers, solvents
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	diaminotoluenes	analogous to nitrobenzene reduction	
n_2 Nitriles + $H_2 \rightarrow \text{primary amines}$	hexanediamine	5-15 MPa/60-130 °C over Raney Ni or Raney Co	starting material for fibers, sour gas scrubbing agent
Miscellaneous reactions $CH_3 \longrightarrow CH_4$	benzene	3 5 MPa/500–650 °C over Cr ₂ O ₃ –Mo ₂ O ₃ –CoO catalyst (Houdry, UOP, Shell, BASF) 10-25 MPa/400-500 °C over Pt-Al ₂ O ₃ –SiO ₂	50% of toluene production further processed to benzene
Xylene isomerization under H ₂ partial pressure	o-/p-xylene	catalysts	terephthalic acid. phthalic acid

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overview of commercially used hydrogenation reactions.

High-purity hydrogen is necessary for the partial or total hydrogenation of fats and oils (for the production of edible fats or for technical purposes). In fat hydrogenation the polyene, triene, and diene fatty acids in their glyceride form are selectively hydrogenated to the corresponding monoene acids.

The industrial production of sugar alcohols, such as sorbitol, xylitol or mannitol from the corresponding sugars is carried out by catalytic hydrogenation. Batch suspension processes using Raney nickel catalysts are mainly employed under reaction conditions of 120–150 °C and 3–7 MPa [8.47].

8.1.6. Hydrogen in Inorganic Synthesis

The catalytic hydrogenation of anthraquinone and its derivatives followed by their autooxidation to yield hydrogen peroxide is the basis of the commercially important process for hydrogen peroxide production (→ Hydrogen Peroxide, p. 447–456). Further important reactions in inorganic chemistry are the production of hydrochloric acid from hydrogen and chlorine (→ Hydrochloric Acid) and the hydroxylamine synthesis (→ Hydroxylamine).

8.2. Hydrogen in Metallurgy

Iron Metallurgy. To reduce iron ore, apart from coke (classical blast furnace process), other reducing agents can be used. For reduction a gas containing hydrogen, carbon monoxide, or mixtures of these is suitable. The reduction gas is produced by steam reforming or partial oxidation of fossil fuels. These "direct reduction" processes (→ Iron, A14, p. 554) yield sponge iron,

which can be melted to give crude iron which is further processed to steel.

The leading direct reduction technologies are the Midrex, the HyL I, and the HyL III process with 90% of the total capacity [8.48]. The hydrogen content of the reducing gas is ca. 40–65 vol% (Midrex, shaft furnace) and 75 vol% (HyL III, retorts). To fully utilize the reduction potential of the gas, carbon dioxide and water vapor are removed and the gas is recycled.

The use of *pure hydrogen* has advantages with respect to the reaction time, the degree of reduction and the texture of the reduced pellets [8.49], but the carbidizing reaction necessary for steel production cannot take place, so that reduction with pure hydrogen has not been able to establish itself.

Nonferrous Metallurgy. Hydrogen is employed as reducing agent and as utility in some powder metallurgy production processes. Table 41 shows the use of hydrogen during the production and handling of various nonferrous metals.

For recovery of copper from its sulfidic ores reduction with hydrogen in the presence of calcium oxide has been suggested [8.50]. The thermodynamically unfavorable position of the hydrogen reduction reaction on metal sulfides is improved by the removal of the developing hydrogen sulfide (as CaS) from the equilibrium mixture.

8.3. Other Uses

Use of the High Temperature of the Oxyhydrogen Flame. The combustion of a stoichiometrical hydrogen—oxygen mixture leads to flame temperatures in the range of 3000–3500 K. Such flames can be used for:

Table 41. Use of hydrogen in the nonferrous metallurgy

Metal	Unit operation	
Copper		Product
Nickel Cobalt	reduction of copper salt solutions under pressure selective reduction during cobalt production reduction of aqueous cobalt salt solutions under pressure (4 MPa, 175 °C)	Cu powder Ni powder Co powder
Molybdenum, tungsten Tantalum Germanium	reduction of the oxides or molybdates and tungstenates reduction of tantalum chloride, TaCl ₅ , in hydrogen plasma reduction of germanium tetroxide, GeO ₄ , at 650 °C	Mo. W powder Ta hydride, Ta powder Ge powder for further
Jranium	reduction of the higher uranium oxides at 650 °C	processing in zone melting UO,